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GROWTH OF BURNING TO DETONATION IN LIQUIDS AND SOLIDS

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ABSTRACT

During the period of this grant a high-speed photographic study has been made of the initiation of explosive liquids (using sparks and impact) and of single crystals of explosive solids (using shock and hot wires). The physical homogenuity of the material has been shown to have a marked effect on its sensitivity. Studies of the fracture of inert solids have shown the importance of specimen geometry and of crack speed on the fragmentation process. Both high-speed photography and ultrasonic methods have been used for the fracture work. One of the main advances has been in the theoretical work on thermal explosion theory.

Table of Contents

(a) Theoretical

Thermal Explosion Theory. The effect of reactant consumption on critical conditions.

We outline below a general theory describing the evolution of temperature with extent of decomposition in an explosive mass suddenly introduced into a high temperature environment. Most of the assumptions common to thermal explosion theory are abandoned and exact expressions for critical Frank-Kamenetski (F-K) temperatures are derived. Our method owes much to that of Adler & Enig (Combustion and Flame, 8, 97, 1964) but is very much more general.

The basic problem. A mass of explosive of volume V, surface area S, has the uniform temperature T and loses heat to its surroundings which are at a temperature To at a rate which is an arbitrary function of (T - To). The rate of heat generation due to chemical reaction is proportional to the product of an arbitrary function of T and an arbitrary function of the fractional extent of decomposition η. When does the system exhibit explosive behaviour?

The rate of heat accumulation is given by:

$$\dot{q}_1 = V\sigma C \frac{dT}{dt} \qquad (1)$$

where σ is the density, t the time, and C the specific heat/unit mass.

The rate of heat loss due to conduction/convection/radiation is

$$\dot{q}_2 = HS(T - To)\, F_1\,(T - To) \qquad (2)$$

where H has the dimensions of a heat transfer coefficient and F_1 is dimensionless.

The rate of heat evolution due to chemical reaction is

$$\dot{q}_3 = - \sigma V q \frac{d\eta}{dt} \tag{3}$$

where q is the total exothermicity/unit mass.

The kinetic law is assumed to have the separable form

$$- \frac{dc}{dt} = - c_o \frac{d\eta}{dt} = k(T, c_o) \Lambda(\lambda) \tag{4}$$

where c is the concentration of reactant (c_o its initial value) and

$$\lambda = 1 - \eta = \frac{c}{c_o} \tag{5}$$

and Λ is an arbitrary function of the fraction of reactant undecomposed.

The temperature dependence of the initial reaction rate is assumed to have the arbitrary form

$$k(T, c_o) = K(c_o) \cdot F_2(T) \exp\left(\frac{-E}{RT}\right) \tag{6}$$

where F_2 is an arbitrary function of temperature.

Our basic equation is the law of conservation of energy

$$\dot{q}_1 = \dot{q}_2 + \dot{q}_3 \tag{7}$$

which we prefer to write in dimensionless form by making the following substitutions:

$$\theta = \frac{E}{RTo^2}(T - To), \quad \varepsilon = \frac{RTo}{E}, \quad \beta = \varepsilon \frac{CTo}{q}$$

$$\psi = \frac{V\sigma q k(To, c_o)/c_o}{HS\varepsilon ToF_1(\varepsilon To)} \tag{8}$$

Equations (1) through (8) give our dimensionless basic equation the form

$$\beta \frac{d\theta}{d} = 1 - \psi^{-1} \frac{\theta_o - \Theta(\theta)}{\Lambda(\lambda)} \tag{9}$$

where β is the reciprocal F-K reduced adiabatic temperature rise and ψ, which we shall call the Semenov criterion, has the critical value $(2.71828\text{---})^{-1}$ in the special case considered in Semenov's classical theory for which:-

$$\varepsilon = 0,\ \beta = 0,\ \bigwedge \equiv 1,\ F_1 = F_2 \equiv 1$$

The function $\textcircled{H}(\theta)$, which we call the F-K function, is given by

$$e^{-\textcircled{H}} = e^{-\theta/1+\varepsilon\theta}\ \frac{F_1(\varepsilon To\theta)}{F_1(\varepsilon To)}\ \cdot\ \frac{F_2(To)}{F_2\ To(1+\varepsilon\theta)} \qquad (10)$$

so that $\textcircled{H}$ has the simple form

$$\textcircled{H} = \frac{\theta}{1+\varepsilon\theta} + \min(1+\varepsilon\theta) - (p-1)\ln\theta \qquad (11)$$

when we adopt the plausible forms:

$$F_1 = \text{const. X } (T - To)^{p-1};\ p = \text{const.} \qquad (12)$$

$$F_2 = \text{const. X } T^m\ ;\ m = \text{const.} \qquad (13)$$

The treatment below applies to the general form (10) of the F-K function. Form (11) merely illustrates the sort of concrete function we have in mind. Conventional thermal explosion theory assumes form (11) with $m = 0$, $p = 1$, $\varepsilon = 0$, i.e., $\textcircled{H} = \theta$.

Particular cases of the kinetic function which are of interest are arbitrary n^{th} order: $\bigwedge = \lambda^n;\ n \geqslant 0$ (14)

autocatalytic: $\bigwedge = \lambda(1-\lambda)$ (15)

Initial conditions. The system starts at some arbitrary temperature θ_o, with no reactant consumption

$$\theta = \theta_o \text{ at } \gamma = 0, \qquad (16)$$

usually $\theta_o < 0$.

A study has been made of the form of curves (9) subject to (16) in the

(θ, η)) plane and a simple analytical method for finding close upper and lower bounds on the value of Ψ for which explosion just fails to occur has been almost entirely elaborated and will be reported in detail later. We show here how to calculate the critical value of the F-K temperature. Curves (9) have an extremum when

$$\Lambda(\lambda)_{extr.} = \Psi^{-1}\, \theta e^{-H} \tag{17}$$

and their curvature (by differentiating (9)) is given by

$$\frac{d^2\theta}{d\eta^2} = -\Psi^{-1} \beta^{-2} \Lambda^{-2}\, e^{-H} Z \tag{18}$$

where $Z = (\Lambda - \Psi^{-1}\, \theta e^{-H})\,(1 - \theta\, H_\theta) + \beta\theta\Lambda_\lambda$ (19)

Differentiating again we find

$$\Psi\, \beta^2 \frac{d^3\theta}{d\eta^3} = \Lambda^{-2}\, e^{-H} \frac{dZ}{d\lambda} + Z \frac{d}{d\lambda}\left(\Lambda^{-2}\, e^{-H}\right) \tag{20}$$

where

$$\begin{aligned} \frac{dZ}{d\lambda} = &-\left[\Lambda - \Psi^{-1}\, \theta e^{-H}\right]\left[\theta\, H_{\theta\theta} + H_\theta\right]\frac{d\theta}{d\lambda} \\ &+ \left[1 - \theta H_\theta\right]\left[\Lambda_\lambda - \Psi e^{-H}(1 - \theta H_\theta)\frac{d\theta}{d\lambda}\right] \\ &+ \beta\left[\theta\Lambda_{,\lambda} + \Lambda_\lambda \frac{d\theta}{d\lambda}\right] \end{aligned} \tag{21}$$

and $\frac{d}{d\lambda}\left(\Lambda^{-2}\, e^{-H}\right) = -\Lambda^{-3}\, e^{-H}\left[\Lambda H_\theta \frac{d\theta}{d\lambda} - 2\Lambda_\lambda\right]$ (22)

The locus of the inflexions of curves (9) is given by

$$Z = 0 \tag{19i}$$

(by equation (18)). Or from (17)

$$\Lambda_{inf.} = \Lambda_{extr.} + \beta\Lambda_{\lambda\, inf.}\, \chi(\theta) \tag{23}$$

where

$$\chi(\theta) = \frac{-\theta}{1 - \theta H_\theta} \tag{24}$$

Now usually $\Lambda_\lambda \geqslant 0$ for all λ, so that (23) means

$$\text{sign}\,(\lambda_{\text{inf.}} - \lambda_{\text{extr.}}) = \text{sign}\,(\chi) \tag{25}$$

The essence of explosive behaviour is that χ is discontinuous, i.e., $1 - \theta\Phi_\theta$ has zeros, so that the inflexion locus has branches lying on alternate sides of the locus of extrema. In all cases of interest we find a region of the (θ, η) within which both $\frac{d\theta}{d\eta}$ and $\frac{d^2\theta}{d\eta^2}$ are positive, and following Adler & Enig we say that the state point must enter this "explosive peninsular" for an explosion to occur. Critical behaviour is observed when a curve (9) touches the inflexion locus, i.e.,

$$\frac{d^2\theta}{d\eta^2} = \frac{d^3\theta}{d\eta^3} = 0 \text{ for criticality} \tag{26}$$

for then the state point just fails to enter the explosive peninsular. Combining (26) and (18) through (22) we find

$$Y = \frac{\Lambda\Lambda_{\lambda\lambda}}{\Lambda_\lambda^2} + \frac{1 + \theta^2\Phi_{\theta\theta}}{(1 - \theta\Phi_\theta)^2} - 1 = 0 \tag{27}$$

$$\text{I} \qquad\qquad \text{II}$$

In general θ_{cr} can be found by eliminating λ from (27) and (19i), but certain special forms of Λ make the process simpler.

If term I in (27) happens to be independent of λ then (27) is immediately an equation in θ_{cr} alone. (Term II however is never independent of θ for forms of Φ of interest to us.)

If we regard $\frac{\Lambda\Lambda_{\lambda\lambda}}{\Lambda_\lambda^2} = K = \text{const.}$ as a differential equation in Λ we find that the only solutions of physical interest are

$$\Lambda = \lambda^n \; ; \; n \geqslant 0; \frac{\Lambda\Lambda\lambda\lambda}{\Lambda_\lambda^2} - 1 = \frac{-1}{n}$$

Thus for the general n^{th} order reaction (n not necessarily integral), and only in the case of a kinetic law of this kind, we find that the critical temperature is given by

$$(1 - \theta \textcircled{H}_\theta)^2 = n(1 - \theta^2 \textcircled{H}_{\theta\theta}) \qquad (28)$$

and in particular θ_{cr} is independent of the parameters ψ , β.

For the standard functions (11) - (13) equation (28) gives a quartic equation in θ which is readily solved (although the resulting expressions are cumbersome).

The case p = n, m = 0, is especially simple and yields

$$\theta_{cr} = \frac{2p}{1 - 2p\epsilon} \qquad (29)$$

For most explosives we have $\epsilon \ll 1$. The solution of (28) and (11) with $\epsilon = 0$ is simply

$$\theta_{cr} = p \pm \sqrt{pn}$$

$$\left(\frac{\partial\theta_{cr}}{\partial\epsilon}\right)_{\epsilon=0} = 2p(2p - m) \pm 2\sqrt{pn}\left[3p - n - m\right] \qquad (30)\ *$$

The values of θ_{cr} given by (28) no longer correspond to explosion when $1 - \theta \textcircled{H}_\theta$ has no zeros (say because ϵ is too large).

Thus there is a termination in explosive behaviour when

$$1 - \theta \textcircled{H}_\theta = 1 + \theta^2 \textcircled{H}_{\theta\theta} = 0 \qquad (31)$$

When θ is eliminated from (31) we thus have an expression for the maximum

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* Only values corresponding to the + sign represent explosion

possible value of ε for explosive behaviour. Equations (31) and (11) give

$$\left.\begin{aligned} \varepsilon &< \frac{2p - m - \sqrt{p(p-m)}}{m^2}; \; m \neq 0 \\ \varepsilon &< \frac{1}{4p} \qquad\qquad\quad ; \; m = 0 \end{aligned}\right\} \text{ for explosion}$$

Much stronger limitations can be imposed upon the value of ε by performing crude integrations of (9). These will be described in the next report.

An important feature in our general examination is the following. Once having located (θ_{cr}, η_{cr}), as we have by equations (19i) and (27), we can assign ψ , β, ε, m, n, p and/or any other parameters that may be involved in F_1 and F_2 and then integrate backwards numerically from the critical point until $\theta_o = 0$ ($\eta = 0$) is reached. In this way we determine

$$\psi_{cr} = \psi_{cr}(\beta, \varepsilon, m, n, p, \theta_o)$$

without resorting to the time-consuming "straddling" techniques.

(b) Liquid Explosives

Work under this heading has been described in the paper "Formation of Cavities and Micro Jets in Liquids and their Role in Initiation and Growth of Explosion" by Bowden and McOnie (Proc. Roy. Soc. in Press).

In the experiments a C_4 continuous access framing camera was used to film the explosion process in thin films of nitroglycerine. Initiation of explosion was by a variety of methods including impact, spark, and exploding foil. The study showed:

(i) that cavities or bubbles in the liquid could change a slow burning

process into a fast detonation. Further, that if cavities or bubbles were not present before the process started, that they could be introduced by stress waves set up by the explosion process itself.

(ii) That there are various situations during the explosion process when fast micro-jets can be produced, and that these fast jets can lead to violent explosion. These jets can be produced, for example, between coalescing drops, when cavities are collapsed by stress waves, or when cavities collapse near a solid surface.

Present work involves a closer study of the collapse of cavities in gels of ranging viscosity.

(c) Solid Explosives

Work on the mechanism of the slow and explosive decomposition of the fulminates was completed this year and the results will be published shortly. In addition to normal methods used to study decomposition and measure electron energy levels in solids, we have carried out X-ray studies to determine how fulminates pack in the unit cell. This was required for an understanding of the decomposition on the molecular level.

(d) Fracture of Inert Crystals

A study of the propagation of fracture in crystalline solids is in progress. The fracture growth has been followed both by high-speed photographic and ultrasonic techniques. This latter method consists essentially of passing a high frequency (say 5×10^6 c.p.s.) beam of ultrasonic waves through a solid at the time of fracture. The oscillating tensions added by the ultrasonic beam modulate the fracture growth causing a faint ripple to be produced on the fracture surface; this acts

as a permanent record of the fracture development, Since the frequency of the imposed waves is known the spacing of the ripples gives an accurate measurement of crack velocity, and acceleration.

The fracture study has shown:

(i) that maximum propagation rates exist for many materials.

(ii) that cracks in glasslike solids tend to branch when they reach a high velocity, but that this branching is suppressed in crystalline solids having well defined cleavage planes, thus enabling cracks in crystalline solids to reach relatively higher velocities (as compared with their stress wave velocities).

(iii) that crack branching can be caused by the interaction of a fracture with a stress wave.

(iv) that the detailed fragmentation of a solid is greatly affected by the duration of the stress pulses involved in the process.

Recently an attempt has been made to photograph down through crystals onto the developing fracture face. This differs from the more conventional approach which observes crack propagation through solids edge-on. This new method has been shown to be feasible; it is more difficult experimentally but has the advantage that the detailed development of all the features on the fracture face can be followed.

References

1. Adler and Enig, Combustion and Flame, 8, 97, 1964

2. Bowdon, F. P. and McOnie M. P., Proc. Roy. Soc. (in Press).

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